

Direct Irradiation of Aryl Sulfides: Homolytic Fragmentation and Sensitized S-Oxidation

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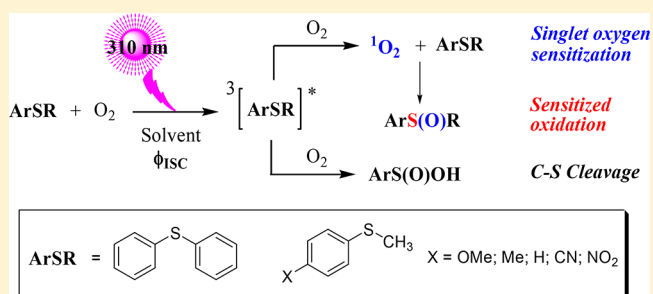
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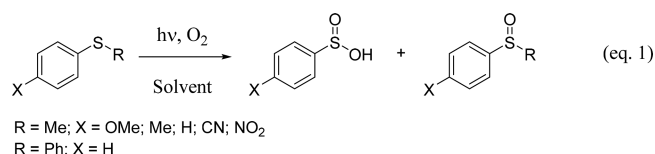
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ABSTRACT: The direct irradiation of diphenyl sulfide and *p*-substituted thioanisoles in the presence of oxygen was investigated by means of both steady state and laser flash photolysis experiments. Two competitive pathways took place from the triplet excited state of thioanisoles, C–S bond cleavage, finally leading to aryl sulfinic acid and sensitized oxidation leading to S-oxidation. Co-oxidation of dodecyl methyl sulfide occurred efficiently implying that an S-persulfoxide intermediate is involved during the sensitized oxidation. On the other hand, triplet state of diphenyl sulfide also showed competitive C–S bond cleavage giving phenyl sulfinic acid and ionization to diphenyl sulfide radical cation that in turn led to diphenyl sulfoxide. The rate constants of the above reactions were determined by time-resolved experiments.



INTRODUCTION

During the past years, our research group has been involved in the study of the photo oxidation of sulfides providing new insight into both the oxygen sensitization and electron transfer oxidation reactions of alkyl and aryl sulfides,¹ through steady-state and laser flash photolysis experiments. In the following, a rather unexpected observation is reported, that is that the direct irradiation (310 nm, with no added energy or electron transfer photosensitizer) of thioanisoles and diphenyl sulfide in oxygen-saturated solutions caused C–S bond cleavage and formation of sulfinic acids, along with S-oxidation of sulfides giving sulfoxides as photoproducts (eq 1).



Two processes appear to occur competitively via aryl sulfonyl radicals (ArS \cdot) which are the reasonable intermediates, and further reaction with molecular oxygen gives the observed aryl sulfinic acids. In the literature, two mechanisms have been reported for the fragmentation of C–S bond. One involves the reaction of oxygen singlet of aryl methyl sulfides (benzyl, benzhydryl, and cumyl aryl sulfides) and occurs efficiently from the S-persulfoxide intermediate through a Pummerer rearrangement affording carbonyl compounds (aldehydes and ketones) as photoproducts in aprotic solvents along with the

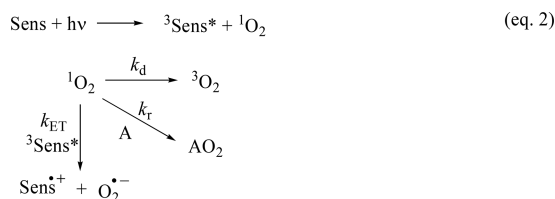
corresponding sulfoxides and sulfones.^{2,1a–c} The second one, involves an electron transfer process releasing aryl thiyl radical and alkyl cation as intermediates,³ as demonstrated by Baciocchi and co-workers, who observed the C–S bond cleavage of aryl 1-methyl-1-arylmethyl sulfide radical cations under steady-state conditions and revealed such intermediates by laser flash photolysis experiments. However, we have earlier demonstrated that diethyl and diphenyl sulfide radical cations do not fragment the C–S bonds and the corresponding sulfoxides were obtained as the photoproducts under electron transfer photosensitization of O₂-saturated solutions.⁴ On the other hand, irradiation (254 nm) of a series of alkyl ethyl sulfides (RSEt) under inert atmosphere, where the second S-bonded substituent R is an alkyl or benzyl group, underwent photo homolysis providing end photoproducts that arose from coupling or disproportionation of the alkyl and thiyl radicals formed with high quantum yields (0.41–0.90).⁵ To summarize, these reports show that C_{sp3}-S bond of sulfides can fragment under different experimental conditions, viz., singlet oxygen sensitization via a sulfide radical cation and from the excited state (singlet or triplet) of a sulfide. Recently, Jiang and co-workers have studied the photochemistry of diphenylquinoxaline derivatives bearing phenyl thioethers as type I photo initiator in photopolymerization experiments and have shown that C_{sp2}-S bond of the thioether moiety fragmented under direct irradiation (365 nm).⁶ Notice that irradiation of diaryl

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sulfoxides is another interesting example of the easy fragmentation of a $C_{sp^2}\text{-S(O)}$ bond. In fact, Jenks and co-workers have studied the photochemistry of diphenyl and ditolyl sulfoxides and α -cleavage is the preferred fragmentation pathway.⁷ Also, the C–S bond strength in $\text{Ph}_2\text{S=O}$ and related compounds has to be around $65 \text{ kcal}\cdot\text{mol}^{-1}$ which is lower than the energies of the singlet ($E_S \approx 90\text{--}100 \text{ kcal}\cdot\text{mol}^{-1}$) and triplet ($E_T \approx 75\text{--}80 \text{ kcal}\cdot\text{mol}^{-1}$) states. Therefore, the $C_{sp^2}\text{-S}$ cleavage of these compounds is markedly exothermic regardless of the excited state involved.

On the other hand, photoinduced S-oxidation is commonly carried out by reaction with singlet oxygen generated by energy transfer from triplet sensitizers.⁸ However, in some cases, it has been demonstrated that such interaction does not occur with unitary efficiency.⁹ In other words, the “chemical” combination of the organic molecule (A) with oxygen is accompanied by purely “physical” decay (eq 2) and further processes, such as the decay of the triplet sensitizer not accompanied by oxygen sensitization and electron transfer.



In general, aryl alkyl (as well as diaryl) sulfides appear to be less reactive toward singlet oxidation and have received less attention than dialkyl sulfides, though the singlet oxygenation of thioanisoles has been considered in mechanistic papers.¹⁰ Addition of protic additives (alcohol and acids), zeolites, and clays provides photo oxidation of sulfides more efficiently.¹¹ Likewise, S-oxidation of alkyl and aryl sulfides could be achieved under electron transfer sensitization in the presence of molecular oxygen and involved sulfide radical cation as the key intermediate.¹² Sulfoxides are generally the main products, but variable amounts of C–S bond cleavage products can also be obtained, depending on the substrate structure.

As it was reported above, we have studied the photochemistry of alkyl sulfides by direct irradiation with wavelength of 254 nm under Ar atmosphere⁵ as well as photosensitized oxidation reactions under energy transfer¹ and electron transfer⁴ conditions of dialkyl, arylalkyl and diaryl sulfides in different solvents and with different photosensitizers. However, according to our knowledge, the possibility of oxidation of sulfides by direct irradiation (310 nm) in the presence of oxygen was not previously investigated making this one of our reason to develop the study. Therefore, based on the preliminary reports mentioned above and considering that the direct irradiation of sulfides was not reported yet encouraged us to do more extensive work for which we chose a series of *p*-substituted thioanisoles and diphenyl sulfide as substrates, as reported below, and examined in terms of product distribution, chemical quenching and laser flash photolysis experiments.

RESULTS

Photo Oxidation of Diphenyl Sulfide. Irradiation of diphenyl sulfide (Ph_2S) in the presence of dyes, such as Rose Bengal (RB), under oxygen flushed solutions causes no chemical change. However, direct irradiation of diphenyl sulfide

in acetonitrile with $\lambda_{\text{exc}} = 310 \text{ nm}$ under oxygen atmosphere caused the generation of diphenyl sulfoxide (12.8%) and phenyl sulfonic acid (32.0%) when Ph_2S is consumed in up to 55% yield. The course of the reaction in MeCN is detailed in Figure 1, where it is apparent that C–S cleavage to form phenyl sulfonic acid is the main process.

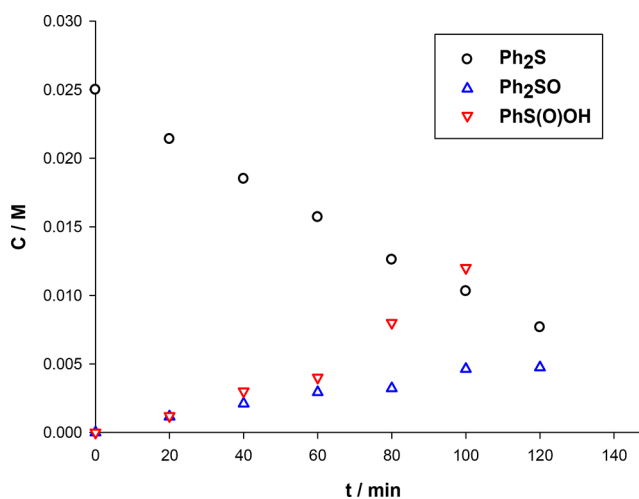


Figure 1. Consumption of diphenyl sulfide (black circles) and formation of phenyl sulfonic acid (red triangles) and diphenylsulfoxide (blue triangles) with reaction time.

The UV–visible spectra of diphenyl sulfide show two absorption bands located at 296 and 320 nm. The first weak absorption band was assigned to the 1L_b state while strong absorption band was assigned to the 1L_a state by comparison with reported data.¹³ Diphenyl sulfide is suitable compound that can absorb the incident light (310 nm) because a maximal overlapping between the 1L_b band and the incident light takes place as it was verified when the recorded UV–visible absorption spectra of a solution of thioanisole in MeCN and the emission spectra of the lamps used (310 nm) were overlaid each other.

The photo oxidation of diphenyl sulfide also occurs in methanol and dichloromethane, a polar protic and an aprotic solvent, respectively, providing the same product distribution. Noteworthy, in any experiment diphenyl sulfone was not formed even at high sulfide conversion. The quantum yields of formation of diphenyl sulfoxide (Ph_2SO) ($\phi_{\text{Ph}_2\text{SO}}$, see Table 1) were also measured and in aprotic solvents the quantum yields are quite similar while in protic solvents, such as methanol, the value is halved.

It is known from the literature that dye photo oxidation of dialkyl and alkylaryl sulfides generates sulfoxides at a noticeably enhanced rate in aprotic solvents in the presence of acids.^{10c,11d} On the contrary, addition of cesium carbonate to the reaction mixture suppressed the formation of sulfoxide (even after a further period in the darkness) as can be seen in Table 1. Likewise, no significant oxidation was detected when diphenyl sulfide was treated with hydrogen peroxide in acetic acid in the darkness.

The role of oxygenated intermediates has been investigated through their oxygen-transfer properties.¹⁵ In the present case, dodecyl methyl sulfide was chosen as an adequate oxygen acceptor because it neither absorbs nor reacts at the excitation wavelength (310 nm). Thus, co-irradiation of diphenyl sulfide (0.010 M) and dodecyl methyl sulfide (0.010 M) in oxygen

Table 1. Direct Photo Oxidation of Diphenylsulfide^a

solvent	sensitizer or additives	conv. (%)	$[\text{Ph}_2\text{SO}]_1/\mu\text{mol min}^{-1}$	$\phi_{\text{Ph}_2\text{SO}}^b$
MeOH	RB (visible light)	0	0	
MeCN		23.0	0.070 (0.120 $\mu\text{mol}\cdot\text{min}^{-1}$ of H^+)	0.048
MeOH		34.4	0.039	0.026
DCM		30.7	0.062	0.041
MeCN	CH_3COOH (2.5×10^{-3} M)	24.1	0.096	
MeCN	CH_3COOH (7.5×10^{-3} M)	11.9	0.073	
MeCN	ClCH_2COOH (5.0×10^{-3} M)	20.3	0.060	
MeCN	34.5 mg Cs_2CO_3	25.0	0	
MeCN	34.5 mg $\text{Cs}_2\text{CO}_3/h\nu$ + 20 min in the darkness	25.0	0	

^aSulfide concentration: 0.010 M. RB = Rose Bengal. ^bActinometer: KI (0.6 M), KIO_3 (0.1 M) and $\text{Na}_2\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.01 M) in water; $\phi(\text{I}_3^-) = 0.38$; $\lambda_{\text{exc}} = 310$ nm.¹⁴ Error: ± 0.001 .

Scheme 1. Co-Irradiation of Diphenyl Sulfide and Dodecyl Methyl Sulfide at 310 nm

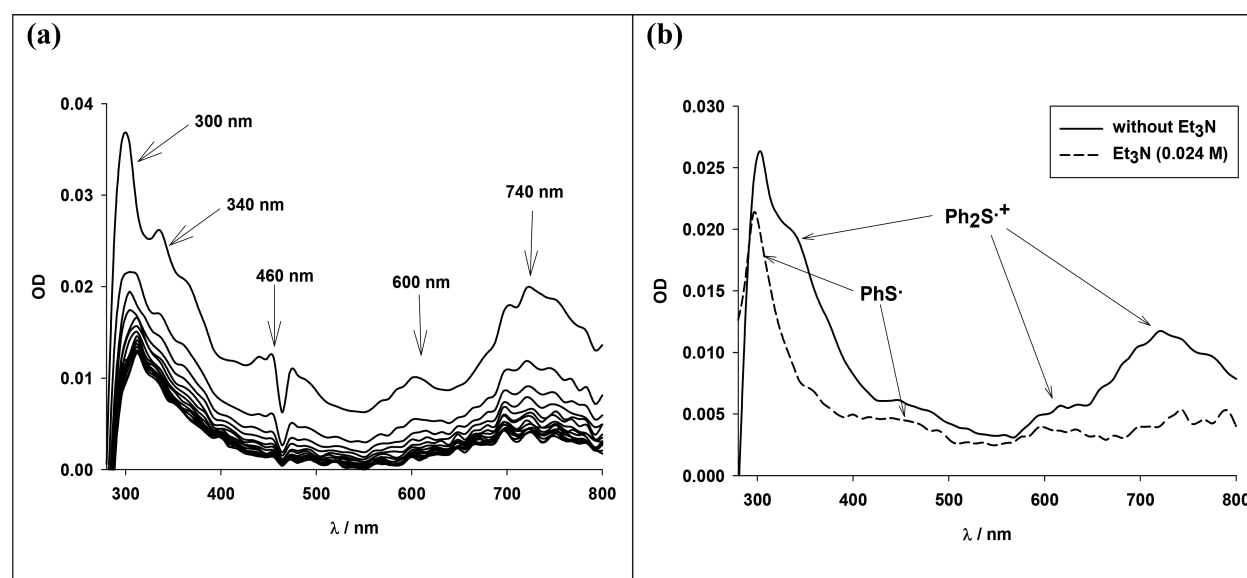
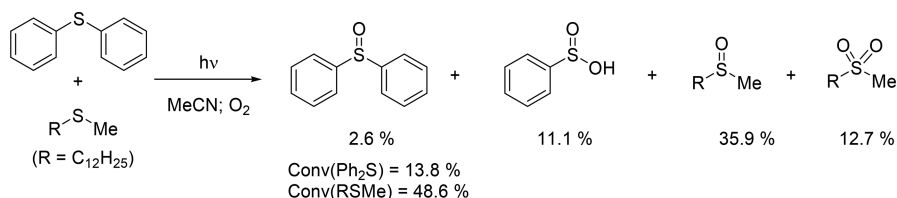


Figure 2. (a) Transient absorption spectra recorded after a laser pulse ($9 \mu\text{s}$; λ_{exc} : 266 nm) of N_2 -saturated acetonitrile solution of diphenyl sulfide (6.03×10^{-4} M). (b) Overlay of transient absorption spectra recorded at $9 \mu\text{s}$ after a laser pulse (λ_{exc} : 266 nm) of N_2 -saturated acetonitrile solution of diphenyl sulfide (6.03×10^{-4} M) in the absence and in the presence of trimethylamine (0.024 M).

saturated MeCN solution caused oxidation of both sulfides (Scheme 1). Under these conditions, dodecyl methyl sulfide was co-oxidized to the corresponding sulfoxide and sulfone supporting that Foote's mechanism via singlet oxygen and persulfoxide is operating.

Time-Resolved Spectroscopy of Diphenyl Sulfide.

Irradiation of diphenyl sulfide in acetonitrile solution with a 266 nm laser pulse under nitrogen atmosphere provides transient absorption spectra (see Figure 2a) showing five characteristic absorption bands located at 300, 340, 460, 600, and 740 nm. Comparison with literature shows that two transient species are responsible for these bands, viz. diphenyl sulfide radical cation and phenyl thiyl radical, with the bands located at 340, 600, and 740 nm attributed to the former, and those at 300 and 460 nm to the latter one.^{16,4} Quenching of the

$\text{Ph}_2\text{S}^{\cdot+}$ radical cation was obtained by addition of triethylamine which is easily oxidized ($E_{\text{ox}}(\text{Et}_3\text{N})$: 0.69 V^{17a} vs $E_{\text{ox}}(\text{Ph}_2\text{S})$: 1.43 V^{17b} (vs SCE)). In fact, in Figure 2b, the bands belonging to the radical cation disappear completely while those of the phenyl thiyl radical remain. This quenching experiment demonstrated that both transient intermediates are simultaneously formed after the laser pulse by two different pathways from the triplet state of diphenyl sulfide: (i) ionization of Ph_2S giving the $\text{Ph}_2\text{S}^{\cdot+}$ and the electron, and (ii) C–S cleavage providing radical PhS^{\cdot} . As reported in the literature, diphenyl sulfide showed a minimal fluorescence emission but a phosphorescence quantum yield of 0.45. The ϕ_p/ϕ_f ratio was also reported and the fluorescence quantum yield was easily estimated as 0.004.¹⁸ Then, we suggest that intersystem crossing to the triplet state of diphenyl sulfide was largely

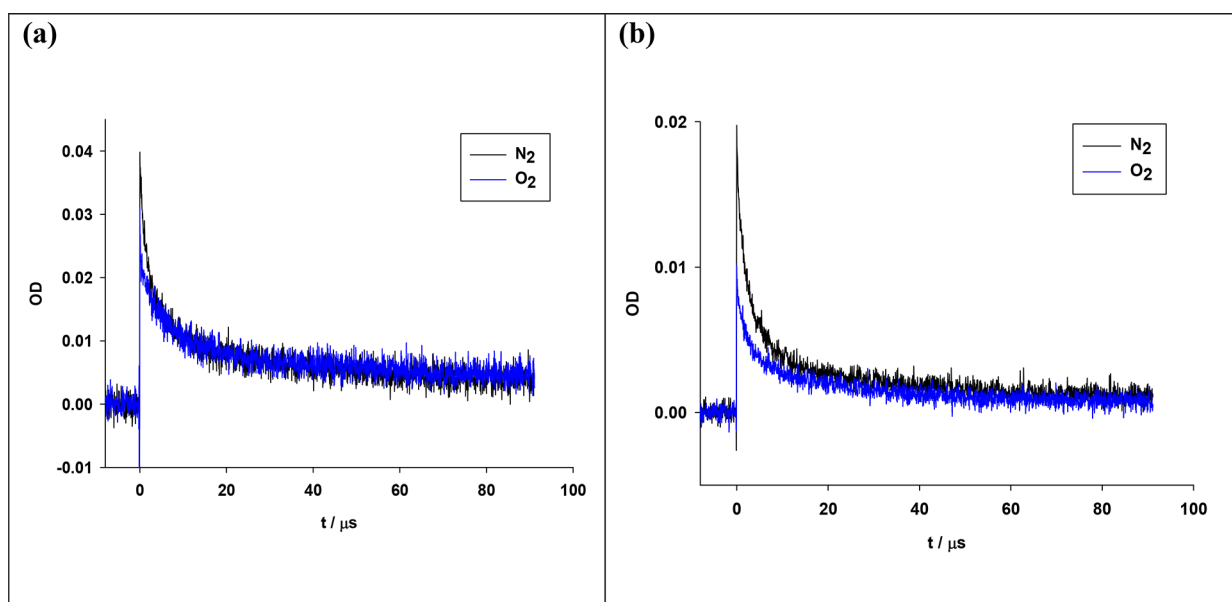


Figure 3. Decay traces of $\text{Ph}_2\text{S}^{\cdot+}$ after a laser pulse (λ_{exc} : 266 nm) of acetonitrile solutions of Ph_2S (6.03×10^{-4} M) recorded at: (a) 740 nm and (b) 450 nm under N_2 and O_2 atmospheres.

predominating taking into account the reported ϕ_f and ϕ_p values and hence, the ionization process as well as the C–S bond cleavage observed after the laser pulse is more likely to proceed from the triplet excited state.

Further, the transient decay traces of both intermediates, $\text{Ph}_2\text{S}^{\cdot+}$ and PhS^{\cdot} , were also recorded at 740 and 460 nm, respectively, where overlapping was minimal, under N_2 and O_2 atmospheres and are shown in Figure 3. Both transients showed nice second-order decays under N_2 -saturated acetonitrile solutions and from the slopes of the linear regression of the reciprocal of the concentration of the transients vs time plots the bimolecular rate constants, k_{BET} and k_{recomb} of $10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$ were obtained (see Table 2).

Table 2. Spectroscopic Data and Bimolecular Rate Constants of Transients $\text{Ph}_2\text{S}^{\cdot+}$ and PhS^{\cdot} ^a

$\text{Ph}_2\text{S}^{\cdot+}$ ($\epsilon_{740} = 5600 \text{ M}^{-1}\cdot\text{s}^{-1}$)	$\lambda_{\text{abs}}/\text{nm}$	N_2	O_2
		$k_{\text{BET}}/\text{M}^{-1}\cdot\text{s}^{-1}$	$k_{\text{ox}}/\text{M}^{-1}\cdot\text{s}^{-1}$
MeCN	340; 740	1.01×10^{10}	3.23×10^7
MeOH	344; 720	1.24×10^{10}	1.04×10^7
PhS^{\cdot} ($\epsilon_{450} = 1800 \text{ M}^{-1}\cdot\text{s}^{-1}$)		N_2	O_2
		$k_{\text{recomb}}/\text{M}^{-1}\cdot\text{s}^{-1}$	$k'_{\text{ox}}/\text{M}^{-1}\cdot\text{s}^{-1}$
MeCN	296; 450	1.01×10^{10}	1.94×10^7
MeOH	304; 448	1.67×10^{10}	8.69×10^6

^aConcentration of diphenyl sulfide: 6.03×10^{-4} M. The concentration of molecular oxygen was 2.42×10^{-3} M in MeCN and 6.58×10^{-3} M in MeOH.

The rate constant k_{BET} was attributed, for the case of diphenyl sulfide radical cation, to the back-electron transfer process between this transient and the ejected electron. Likewise, for the case of phenyl sulfide radical, the rate constant k_{recomb} represented the recombination process of the radicals formed after the C–S fragmentation in the solvent cage.

On the other hand, the decay traces of transients $\text{Ph}_2\text{S}^{\cdot+}$ and PhS^{\cdot} showed a pseudo-first order decay under oxygen

atmosphere indicating that both transients reacts efficiently with molecular oxygen. After fitting analysis of the data the pseudo-first rate constants were obtained and a second-order rate constant of 10^6 – $10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$ was calculated by considering the concentration of O_2 solubilized in each of the solvents used (see Table 2).

Direct Photo Oxidation of *para*-Substituted Thioanisoles. The irradiation was extended to thioanisole and some of its *para*-substituted derivatives. As it was observed for diphenyl sulfide, thioanisole derivatives also show two typical absorption bands located around 260 and 300 nm. The first weak absorption band was assigned to the $^1\text{L}_b$ state while strong absorption band was assigned to the $^1\text{L}_a$ state by comparison with reported data.¹³ The $^1\text{L}_b$ band of thioanisoles overlaps with the incident light (310 nm) and the absorption process occurs efficiently promoting the photoreaction. The course of the reaction was monitored for thioanisole in MeCN under oxygen atmosphere (see Figure 4) and showed that acidity

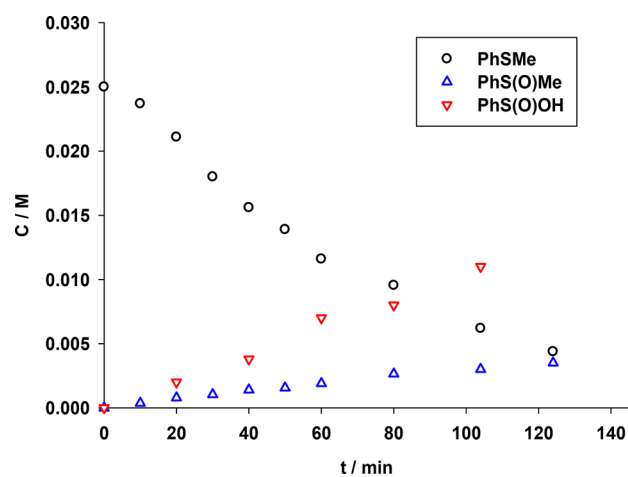


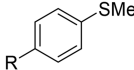
Figure 4. Consumption of thioanisole (black circles) and formation of phenylsulfonic acid (red triangles) and phenyl methyl sulfoxide (blue triangles) vs irradiation time.

Table 3. Direct Photo Oxidation of Thioanisole^a

solvent	sensitizer or additives	conv. (%)	[PhS(O)Me] ₁ /μmol min ⁻¹	φ _{PhS(O)Me} ^b
MeOH	RB (visible)	25.5	0.136	
MeCN		35.2	0.033	0.022
MeOH		30.5	0.189	0.124
DCM		48.5	0.045	0.019
MeCN	acetone (8:2)	27.2	0.052	
MeCN	ClCH ₂ COOH (2.5 × 10 ⁻³ M)	25.7	0.174	
MeCN	ClCH ₂ COOH (5.0 × 10 ⁻³ M)	27.2	0.213	
MeCN	Cs ₂ CO ₃ (34 mg)	36.0	0	

^aSulfide concentration: 0.010 M. RB = Rose Bengal. ^bActinometer: KI (0.6 M), KIO₃ (0.1 M) and Na₂B₂O₇·10H₂O (0.01 M) in water; φ(I₃⁻) = 0.38; λ_{exc} = 310 nm.¹⁴

Table 4. Direct Photo Oxidation of *p*-Substituted Thioanisole Derivatives^a

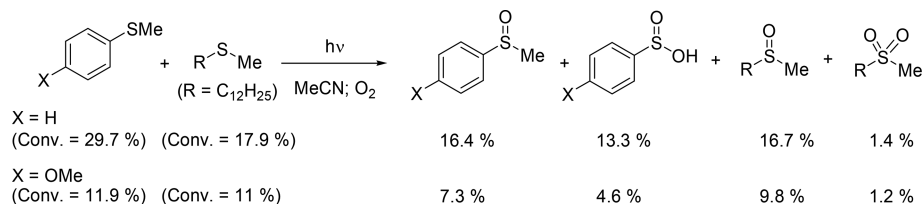
	Solvent	Conv. (%)	[SO] ₁ / μmol min ⁻¹	φ _{SO} ^c
MeO	MeCN	20.1	0.118	0.077
	MeCN ^b	22.3	0	---
	DCM	25.2	0.119	0.078
	MeOH	25.9	0.055	0.036
Me	MeCN	26.7	0.123	0.080
	DCM	45.3	0.071	0.046
	MeOH	10.6	0.131	0.086
H	MeCN	35.2	0.033	0.022
	MeCN ^b	36.0	0	---
	DCM	48.5	0.045	0.024
	MeOH	30.5	0.189	0.124
CN	MeCN	21.1	0.041	0.017
	DCM	33.2	0.077	0.050
	MeOH	11.2	0.027	0.018
NO ₂	MeCN	8.0	0.010	0.007
	DCM	14.0	0.023	0.015
	MeOH	7.0	0.007	0.005

^aSulfides concentration: 0.010 M. SO = sulfoxides. ^bCarried out in the presence of Cs₂CO₃ (34 mg). ^cActinometer: KI (0.6 M), KIO₃ (0.1 M) and Na₂B₂O₇·10H₂O (0.01 M) in water; φ(I₃⁻) = 0.38; λ_{exc} = 310 nm.¹⁴

generation (formation of phenylsulfonic acid) was even more predominating over the oxidation (formation of phenyl methyl

sulfoxide). A similar photochemical behavior was observed when the photoreaction of thioanisole was carried out in

Scheme 2. Co-Irradiation of Thioanisoles and Dodecyl Methyl Sulfide



methanol and in dichloromethane under oxygen atmosphere. The results are collected in Table 3. The rate of formation of phenyl methyl sulfoxide in methanol is four times higher than in aprotic solvents (MeCN and dichloromethane), which showed quite similar values in the last two solvents. Noteworthy, the rate of formation of sulfoxide under direct irradiation of thioanisole in methanol shows the same order of magnitude of that obtained under Rose Bengal sensitized conditions indicating that proticity of the solvent enhances the formation of the sulfoxide.^{11d}

As it is apparent in Table 3, direct irradiation of thioanisole in MeCN took place also in the presence of an external triplet energy sensitizer (acetone) and was accelerated by the addition of acids such as chloroacetic acid (compare the rate in the presence of acid (5×10^{-3} M), $0.213 \mu\text{mol}\cdot\text{min}^{-1}$ with that in neat MeCN, $0.033 \mu\text{mol}\cdot\text{min}^{-1}$). On the other hand, no oxidation to sulfoxide took place in the presence of bases, but the cleavage to the phenyl sulfinate was maintained.

The direct irradiation of *para*-substituted thioanisoles was carried out under the same conditions and the results are collected in Table 4. As is apparent, the photo oxidation of these thioanisoles occurred in protic and aprotic solvents and a marked substituent effect was observed. Thus, electron-donating substituted thioanisoles made the photo oxidation faster. However, the C–S cleavage of thioanisoles to give the corresponding aryl sulfinic acids remaining competitive also in the presence of a base such as Cs_2CO_3 where no photo oxidation took place (see for example in Table 4, *p*-methoxythioanisole in MeCN in the presence of Cs_2CO_3).

The photocooxidation of thioanisole and *p*-methoxythioanisole in the presence of dodecyl methyl sulfide was likewise explored and gave results similar to those obtained for Ph_2S (see Scheme 2). Thus, a common intermediate is formed that oxidizes the oxygen acceptor dodecyl methyl sulfide.

On the basis of the above data collected for thioanisole and *p*-substituted thioanisole, steady-state and time-resolved spectroscopies were further studied to shed some light on the reaction mechanism and, particularly, on the S-oxidation and C–S fragmentation pathways of these substrates.

Steady-State and Time-Resolved Spectroscopy of Thioanisoles: The Oxidation Pathway. The fluorescence emission spectra of thioanisoles were recorded in MeCN using a solution of 4-chloroanisole as fluorescence actinometer. All the substrates showed a minimal fluorescence emission and the fluorescence quantum yields are collected in Table 5. With these molecules, intersystem crossing to the triplet excited state was in all case largely dominating. Time-resolved experiments were then carried out. In every case an emission spectrum identical to that obtained by using perinaphthenone, and attributed to the singlet oxygen phosphorescence, was obtained in MeCN. Comparison of the zero time intensity of the signal allowed measuring the production of singlet oxygen (ϕ_Δ) compiled in Table 5, which turned out to be around 0.15.

Table 5. Fluorescence Quantum Yield and Singlet Oxygen Quantum Yield (ϕ_Δ) of Thioanisole and *p*-Substituted Thioanisole Derivatives Measured in MeCN

	Atmosphere	ϕ_f^a	ϕ_Δ^b
MeO	Ar	0.008	0.10
	O ₂	0.007	
Me	Ar	0.006	0.17
	O ₂	0.005	
H	Ar	0.004	0.15
	O ₂	0.003	
CN	Ar	4×10^{-4}	0.16
	O ₂	3×10^{-4}	
NO ₂	Ar	Not detected	0.15

^aActinometer: acetonitrile solution of 4-chloroanisole under Ar atmosphere; $\phi_f = 0.019$;¹⁹ Error: ± 0.002 . ^bValues relative to acetonitrile solution of perinaphthenone; $\phi_\Delta = 0.95$;²⁰ Error: ± 0.002 .

Because the ϕ_Δ values obtained for the thioanisole derivatives are less than unitary, a number of mechanisms have been considered for rationalizing this behavior that include chemical combination, energy transfer and fragmentation.

Additionally, time-resolved experiments have been carried out using laser flash photolysis and the decay of the phosphorescence emission of singlet oxygen in the presence of the thioanisole derivatives was further analyzed in MeCN. Figure 5 shows typical decay traces of the emission of singlet oxygen in the presence of *p*-methoxythioanisole and *p*-cyanothioanisole, respectively. The decay of the singlet oxygen phosphorescence emission at 1230 nm in the presence of the thioanisoles was well fitted by a biexponential decay by using a laser pulse with an energy of *ca* 4 mJ and a $\lambda_{\text{exc}} = 266$ nm, thus giving two observed lifetime values, τ_d and τ_{ox} with the former much larger than the latter one.

Two competitive pathways of deactivation of the singlet oxygen produced are attributed to the physical deactivation of the singlet oxygen (k_d) and to the reaction between singlet oxygen and the nucleophilic sulfide (k_{ox}) to give the corresponding sulfoxide, respectively. The spectroscopic data are collected in Table 6. The large values obtained were assigned to the physical deactivation of the singlet oxygen (τ_d) by comparison of the singlet oxygen decay value in the absence

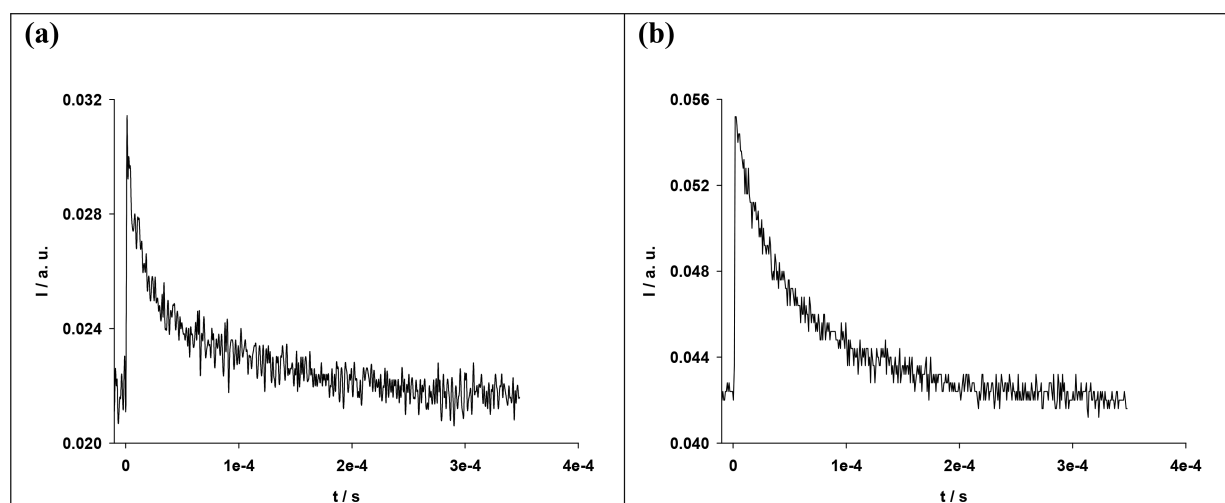
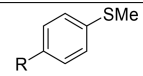


Figure 5. Singlet oxygen phosphorescence emission (λ_{max} : 1230 nm) decay traces in the presence of: (a) *p*-methoxythioanisole and (b) *p*-cyanothioanisole.

Table 6. Lifetimes (τ_{d} and τ_{ox}) of Singlet Oxygen and $\tau_{\text{d}}/\tau_{\text{ox}}$ Ratio in the Presence of Thioanisole and *p*-Substituted Thioanisole Derivatives Measured in MeCN at Room Temperature

	$\tau_{\text{d}}^{\text{a}} / \mu\text{s}$	$\tau_{\text{ox}}^{\text{a}} / \mu\text{s}$	$\tau_{\text{d}}/\tau_{\text{ox}}^{\text{b}}$
OMe	134.0	12.7	10.6
Me	115.0	18.2	6.3
H	84.2	12.5	6.7
CN	79.2	16.1	4.9
NO ₂	71.8	23.0	3.1

^aErrors = ± 0.1 . ^bThe ratio $\tau_{\text{d}}/\tau_{\text{ox}}$ is equal to the ratio $k_{\text{ox}} \cdot [\text{ArSMe}]/k_{\text{d}}$.

of sulfides, which is 86.9 μs in MeCN. Then, the small values collected in the table were attributed to the reaction between

thioanisoles and singlet oxygen. In the same table the $\tau_{\text{d}}/\tau_{\text{ox}}$ ratio which is equal to the ratio of $k_{\text{ox}} \cdot [\text{ArSMe}]/k_{\text{d}}$ was also included. The thus calculated values showed the expected trend of the substituent effect, electron-donating substituents enhance the oxidation rate constant while electron-withdrawing substituents lower it and rather favor the physical deactivation of singlet oxygen.

The C–S Fragmentation Pathway of Thioanisoles.

Laser flash photolysis of N₂- and O₂-saturated acetonitrile solutions of thioanisoles were carried out with a laser pulse of λ_{exc} : 266 nm and transient absorption spectra were obtained. The absorption spectra showed two characteristic bands located around 295–310 nm and 450–530 nm as can be seen in Figure 6 for *p*-methoxy and *p*-methyl thioanisoles in MeCN under N₂ atmosphere.

Addition of radical cation scavengers such as triethylamine or NaN₃ caused no change of the transient absorption spectra and thus, the spectra can be assigned to aryl thiyl radicals (ArS \cdot). Similar spectra have been obtained by laser flash photolysis and

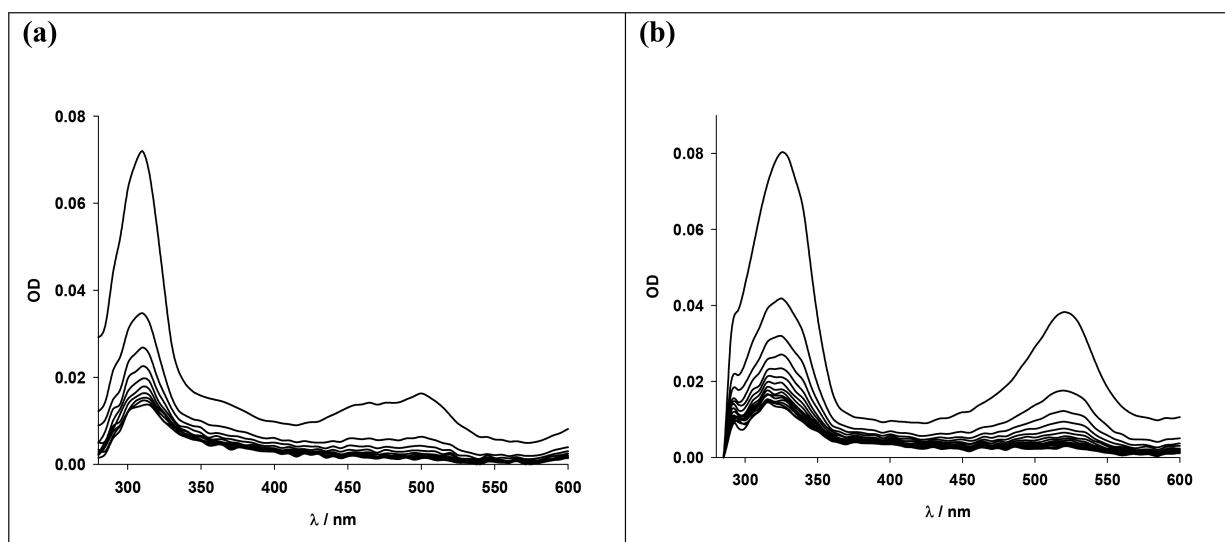


Figure 6. Transient absorption spectra recorded after a laser pulse (9 μs ; λ_{exc} : 266 nm) of N₂-saturated acetonitrile solution of (a) *p*-methylthioanisole and (b) *p*-methoxythioanisole (6.03×10^{-4} M).

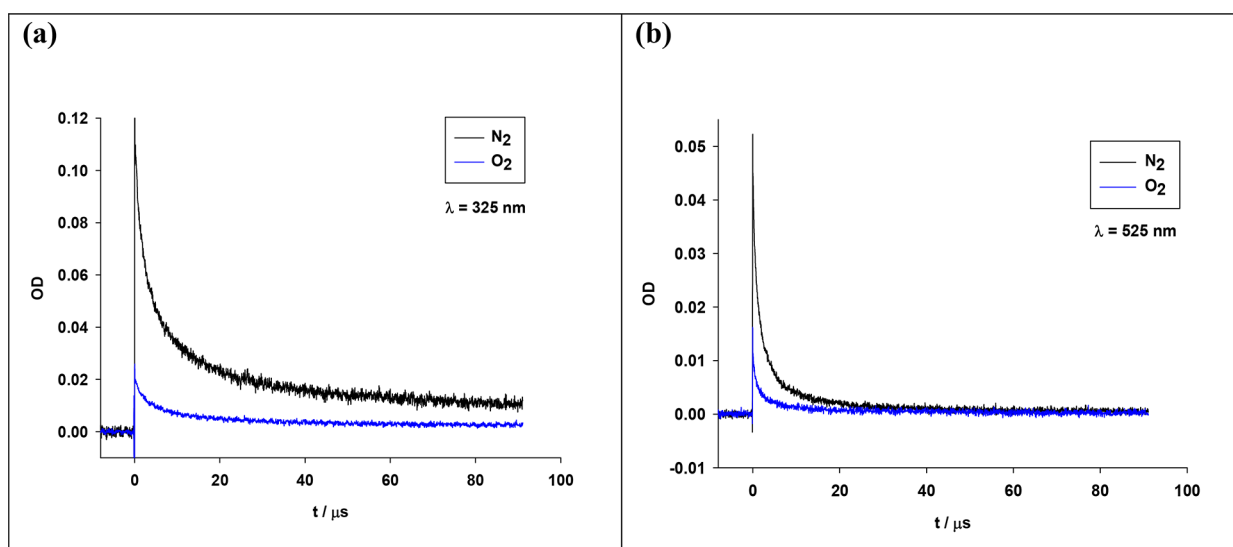


Figure 7. Decay traces of aryl thiyl radical ($\text{ArS}\cdot$) after a laser pulse ($\lambda_{\text{exc}}: 266 \text{ nm}$) of acetonitrile solutions of thioanisoles ($6.03 \times 10^{-4} \text{ M}$) recorded at: (a) 325 nm for *p*-methoxythioanisole and (b) 525 nm for *p*-cyanothioanisole under N_2 and O_2 atmospheres.

pulse radiolysis.²¹ Therefore, C–S cleavage process is a competitive pathway for thioanisoles.

The transient decay traces of such radical were recorded under N_2 and O_2 atmospheres as shown in Figure 7 for *p*-methoxythioanisole and *p*-cyanothioanisole, respectively. Under N_2 the transient decay traces showed nice second-order decays from which, after linear regression fittings, bimolecular rate constants (k_{recomb}) were obtained (rather independent of the substituent, 1 to $2 \times 10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$) and are collected in Table 7. Such rates (k_{recomb}) were attributed to the recombination rate constants of the radicals formed after the C–S fragmentation from the triplet state of thioanisoles.

Table 7. Bimolecular Rate Constants of Transient Aryl Thiyl Radicals in MeCN^a

thiyl radicals	N_2 $k_{\text{recomb}}/\text{M}^{-1}\cdot\text{s}^{-1}$	O_2 $k'_{\text{ox}}/\text{M}^{-1}\cdot\text{s}^{-1}$
<i>p</i> -MeOPhS·	9.82×10^9	3.06×10^7
<i>p</i> -MePhS·	2.06×10^{10}	4.17×10^7
PhS·	1.39×10^{10}	4.05×10^7
<i>p</i> -CNPhS·	9.31×10^9	3.29×10^7
<i>p</i> -NO ₂ PhS·	1.43×10^{10}	1.36×10^6

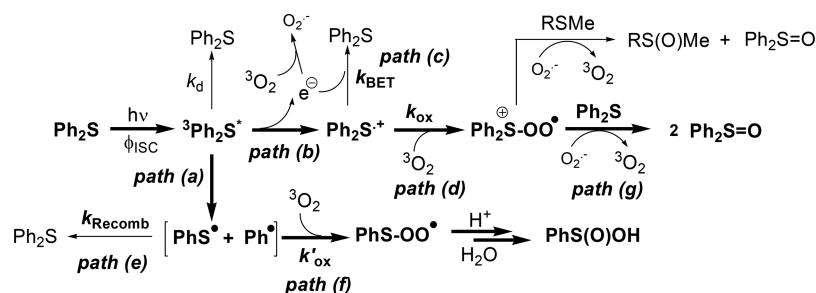
^aConcentration of thioanisoles: $6.03 \times 10^{-4} \text{ M}$. The concentration of molecular oxygen was $2.42 \times 10^{-3} \text{ M}$ in MeCN.

On the other hand, O_2 -saturated acetonitrile solutions of thioanisoles afforded pseudo-first order decay traces that, after fitting analysis, second-order rate constants (k'_{ox}) of $10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$ were calculated taking into account the concentration of O_2 dissolved in MeCN ($2.42 \times 10^{-3} \text{ M}$). These data are also collected in Table 7. The change in the kinetic profile of the decay traces from N_2 to O_2 atmospheres supports that aryl thiyl radicals react smoothly with molecular oxygen to give aryl sulfonyl peroxy radicals in competition with recombination. Another feature observed when comparing the decay trace profiles obtained in N_2 - and O_2 -saturated solutions is that molecular oxygen diminishes the optical density at time-zero after the laser pulse from one-fifth to one-sixth fold indicating that molecular oxygen quenches efficiently the triplet excited state of the thioanisoles.

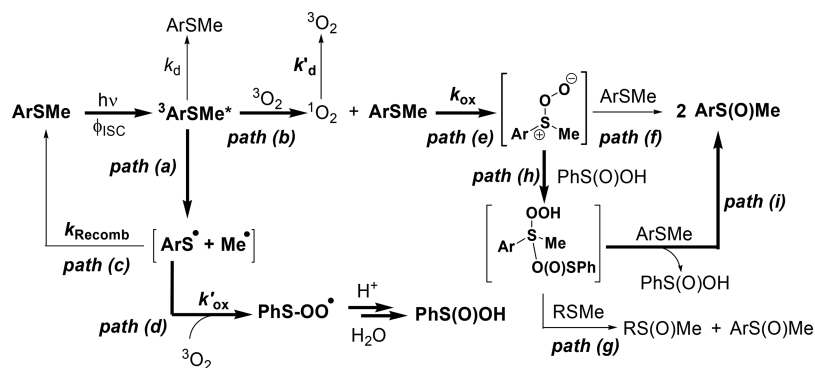
DISCUSSION

Direct Irradiation of Diphenyl Sulfide. As hinted above diphenyl sulfide reacted efficiently upon direct irradiation (310 nm) in MeCN, MeOH, and DCM under oxygen atmosphere. Steady-state and laser flash photolysis experiments reported above give credence to the mechanism shown in Scheme 3. Upon irradiation of Ph_2S at 310 nm efficient population of the triplet state is achieved. Two main pathways compete with the physical deactivation (k_d ; Scheme 3) of the triplet state, viz. (i) homolytic C–S bond fragmentation (path (a)) giving intermediate phenyl thiyl radical ($\text{PhS}\cdot$) that finally evolves to

Scheme 3. Reaction Mechanism Proposed for Direct Irradiation of Diphenyl Sulfide



Scheme 4. Proposed Reaction Mechanism for Direct Irradiation of Thioanisoles



phenyl sulfenic acid (main photoproduct under O_2) and (ii) ionization of diphenyl sulfide to diphenyl sulfide radical cation ($Ph_2S^{\cdot+}$) (path (b)) evolving in the presence of molecular oxygen to Ph_2SO . Laser flash photolysis experiments of N_2 - and O_2 -saturated acetonitrile solution of Ph_2S with $\lambda_{exc} = 266$ nm gave the transient absorption spectra of both intermediates, viz. $PhS\cdot$ and $Ph_2S^{\cdot+}$, which were formed simultaneously at 9 μs after the laser pulse (see Figure 2).

Under N_2 , recombination of the radical gave back Ph_2S (path (e)) with a second order rate constant (k_{recomb}) of $1.01 \times 10^{10} M^{-1}\cdot s^{-1}$ in MeCN and $1.67 \times 10^{10} M^{-1}\cdot s^{-1}$ in MeOH. Likewise, diphenyl sulfide radical cation formed by ionization of triplet Ph_2S (path (b)) under N_2 decays by back-electron transfer process (path (c)) in both solvents, with a second order rate constant (k_{BET}) of $10^{10} M^{-1}\cdot s^{-1}$ (see Table 2).

On the other hand, laser experiments carried out under O_2 atmosphere showed that both transient species, $PhS\cdot$ and $Ph_2S^{\cdot+}$, react smoothly with molecular oxygen with bimolecular rate constants (k_{ox} and k'_{ox}) ranging from 10^6 to $10^7 M^{-1}\cdot s^{-1}$ (see path (f) and path (d) in Scheme 3). In the case of phenyl thiyl radical ($PhS\cdot$) reaction with molecular oxygen gives intermediate phenyl sulfonyl peroxy radical ($PhSOO\cdot$) that, in the presence of adventitious water in the solvent, evolves finally to the phenyl sulfenic acid which is the main photoproduct detected under steady-state experiments. Likewise, diphenyl sulfide radical cation ($Ph_2S^{\cdot+}$) reacts with molecular oxygen to provide the persulfoxide radical cation intermediate as shown in path (d) that finally evolves to diphenyl sulfoxide ($Ph_2S=O$), the other photoproduct detected under steady-state experiments. Dialkyl and diaryl sulfides radical cation are prone to react with molecular oxygen as has been early demonstrated by laser flash photolysis forming the corresponding sulfoxides as photoproducts.⁴ Other related reactive oxygen species (ROS), such as singlet oxygen and superoxide ion, can be involved in the overall processes, the superoxide ion may be formed by trapping the electron ejected from Ph_2S . The fate of this anion has been the subject of some controversy in the case of sulfides, and both back electron transfer between $O_2^{\cdot-}$ and $R_2S^{\cdot+}$ as well as addition reaction of $O_2^{\cdot-}$ with $R_2S^{\cdot+}$ have been proposed.^{4,22} The role of superoxide ion is more precisely indicated by the decay traces of $Ph_2S^{\cdot+}$ measured at 740 nm under oxygen atmosphere which shows a pseudo-first order kinetics in all the solvents studied. If a direct reaction of $O_2^{\cdot-}$ with $Ph_2S^{\cdot+}$ was the primary oxidation pathway, second-order kinetics would be observed which is not the case in our experiments. Therefore, $O_2^{\cdot-}$ has a role, but does not add to the diphenyl sulfide radical cation. A reasonable alternative is that $O_2^{\cdot-}$ operates as electron carrier in the reduction of $Ph_2SO\cdot^+$ (path (g), Scheme 3) in

the presence of a molecule of diphenyl sulfide to give diphenyl sulfoxide.

An active role of singlet oxygen has been previously excluded by Baciocchi for *N*-methylquinolinium-mediated electron-transfer oxidation of sulfides,²² because the reaction is faster than expected. In our case, a comparison between the bimolecular rate constant (k_r) between Ph_2S and singlet oxygen ($3.9 \times 10^4 M^{-1}\cdot s^{-1}$)²³ and the values shown in Table 2, highlights that this process does not compete efficiently with the reaction of $Ph_2S^{\cdot+}$ and molecular oxygen. Furthermore, in our experimental conditions no Ph_2SO_2 was formed, a photoproduct that was usually observed under singlet oxygen sensitization of sulfides.¹ Therefore, we excluded reaction of singlet oxygen with Ph_2S from the reaction mechanism as a competitive oxidative pathway.

As far as we know, the homolytic fragmentation of the $C_{sp^2}\text{-S}$ bond from the triplet state of diphenyl sulfide is reported here for the first time. However, this kind of fragmentation has been recently reported by Jiang and co-workers⁶ and has been also observed with aryl alkyl sulfoxides.⁷ In the case of aryl alkyl sulfide radical cations the homolytic fragmentation of $C\text{-S}$ bond occurs efficiently releasing aryl thiyl radicals and the corresponding carbocations⁸ but the $C\text{-S}$ bond of diphenyl sulfide radical cation does not fragment as it was early suggested.⁴ In fact, our results confirm $Ph_2S^{\cdot+}$ behavior. Upon laser flash photolysis excitation of a N_2 -saturated solution of Ph_2S in MeCN both $PhS\cdot$ and $Ph_2S^{\cdot+}$ transients are formed simultaneously but, addition of triethylamine as a radical cation quencher to the solution, inhibits the formation of $Ph_2S^{\cdot+}$ but not the formation of $PhS\cdot$. Therefore, we can conclude that these results demonstrate that (i) $Ph_2S^{\cdot+}$ does not fragment to $PhS\cdot$ and Ph^+ and (ii) $C_{sp^2}\text{-S}$ homolytic fragmentation occurs competitively from the triplet state of Ph_2S and not from the $Ph_2S^{\cdot+}$.

Direct Irradiation of Thioanisoles. As in the case of diphenyl sulfide direct irradiation (310 nm) of thioanisoles provided aryl sulfenic acid as the main photoproduct along with the corresponding sulfoxides under oxygen atmosphere in MeOH, MeCN, and DCM (see Table 4 and Figure 4). Based on steady-state and laser flash photolysis experiments described above we propose the reaction mechanism for the direct irradiation of the thioanisoles shown in Scheme 4. All the thioanisoles showed very low fluorescence quantum yields ($\phi_f < 0.008$; see Table 5) and intersystem crossing to the triplet state in all cases predominated. Thus, direct excitation of these substrates at 310 nm populated efficiently the triplet state which is the photo reactive state involved in the photoreaction. In the case of thioanisoles, two distinctly and competitive

pathways occurred: homolytic C–S fragmentation (path (a); Scheme 4) and singlet oxygen sensitization (path (b); Scheme 4). Irradiation of N₂-saturated acetonitrile solutions of thioanisoles with a laser pulse (266 nm) afforded transients absorption spectra which were assigned to the aryl thiyl radical demonstrating that C–S homolytic fragmentation occurred efficiently (see, for example, Figure 6 for the cases of *p*-methyl- and *p*-methoxythioanisoles). Noteworthy, no radical cation transients of thioanisoles were detected in laser experiments indicating that no ionization occurred after the laser pulse as it was observed for the case of diphenyl sulfide. This means that C_{sp3}–S cleavage in thioanisoles competes efficiently with the ionization process despite the fact that thioanisoles have oxidation potentials ranging between 1.13 to 1.70 V vs SCE^{10c} and are susceptible to oxidation under laser flash photolysis conditions.

The absorption decay traces of the aryl thiyl radicals were also recorded in MeCN under N₂ atmosphere and showed clean second-order kinetics (k_{recomb}) of 10⁹ to 10¹⁰ M⁻¹·s⁻¹ (see Table 7 and Figure 7) which were assigned to the recombination process of the radical species formed in-cage after the laser pulse (path (c); Scheme 4). When the same experiments were carried out under O₂-saturated acetonitrile solutions a noticeable change in the decay traces of the transients were observed (see Figure 7). In fact, pseudo-first order kinetics was obtained for all the thioanisoles studied and bimolecular rate constants (k'_{ox}) of 10⁷ M⁻¹·s⁻¹ were calculated using the concentration of dissolved molecular oxygen in MeCN of 2.42 × 10⁻³ M (see Table 7). This behavior was easily attributed to the reaction of molecular oxygen with aryl thiyl radical (path (d); Scheme 4) giving phenyl sulfonyl peroxy intermediate PhSOO· that evolve to the phenyl sulfonic acid in the presence of adventitious water in the solution. Noteworthy, pathways (a) and (d) and subsequently formation of phenyl sulfonic acid clearly describes the results obtained under steady-state and time-resolved experiments for the thioanisoles studied.

On the other hand, thioanisoles behaved as smooth singlet oxygen sensitizers when irradiated under oxygen atmosphere (path (b); Scheme 4) with a production of singlet oxygen (ϕ_{Δ}) of ca. 0.10–0.15 (see Table 5). Two competitive pathways take place: (i) physical deactivation of the singlet oxygen (k_{d}) to the ground state and, (ii) reaction of ¹O₂ with nucleophilic thioanisoles to give the corresponding S-persulfoxide intermediates (path (e) in Scheme 4), as supported by the analysis of the decay curves of the phosphorescence emission of singlet oxygen with two distinct lifetime values, τ_{d} and τ_{ox} (Table 6). Thus, τ_{d} described the physical decay of singlet oxygen while τ_{ox} refers to the reaction between singlet oxygen and the nucleophilic thioanisoles (k_{ox} in path (e); Scheme 4). S-persulfoxide intermediates were formed with thioanisoles. Reaction of the intermediate with a molecule of thioanisole afforded the corresponding thioanisole sulfoxides (path (f)). Formation of S-persulfoxide intermediate occurs during singlet oxygen photo sensitization of sulfides as have been reported in the literature.^{10,14,24} However, protonation of S-persulfoxide intermediate during the photoreaction takes place and the oxidant intermediate is more likely to be the S-hydropersulfoxide intermediate (path (h) in Scheme 4). The catalytic effect of acids on the photosensitized oxidation of sulfides is well documented in the literature and the intermediate S-hydropersulfoxide has been proposed.^{10c,11d} This intermediate is also a good oxidant species that evolves to the corresponding

sulfoxide releasing the acid catalyst, in our case, the phenyl sulfonic acid (path (i); Scheme 4). It is clearly that the acidity in all the solvents studied arises from the formation of phenylsulfonic acid during the irradiation. Thus, efficient protonation of the S-persulfoxide intermediate accelerates the oxidation process and promotes high regio selectivity in favor of the sulfoxide over the sulfone (compare the data in Table 3 of the rate of formation of sulfoxide in MeCN with the increasing amounts of ClCH₂COOH). In fact, no sulfones were detected during direct irradiation of thioanisoles, a typical side product formed under singlet oxygen sensitization of sulfides.^{1,2,3a} Sulfone derivatives are formed from a S-hydroxypersulfonium ylide as it was early reported by Sawaki^{10b} and later by us in the photosensitized oxidation of 4-substituted thioanisoles.^{10c} However, this ylide that is formed during the irradiation is inhibited under the acidic condition of the photoreaction and sulfones are not formed which is in agreement with our observations. Therefore, we suggest that the formation of sulfoxides is more likely to proceed by the sequence of path (h) and path (i) (see Scheme 4) under acid catalysis than through path (f). Further, the S-persulfoxide intermediate is a good oxidant species and is able to co-oxidize dodecyl methyl sulfide when is added to the reaction mixture. In fact, direct irradiation of a solution of the thioanisole in the presence of dodecyl methyl sulfide (RSM_e in Scheme 4), which does not absorb at 310 nm, co-oxidation take place (path (g)) and both sulfoxides are formed in good yields (see Scheme 2).

CONCLUSIONS

The photochemical reaction of diphenyl sulfide and *p*-substituted thioanisoles examined in the present paper take place, at least, through two competitive reaction mechanisms, S–C bond cleavage and S-oxidation occurring in polar and nonpolar solvents. Photo homolytic fragmentation of C_{sp2}–S (for diphenyl sulfide) and C_{sp3}–S (for thioanisoles) give the corresponding aryl thiyl radicals (ArS·) which are characterized by laser flash photolysis spectroscopy (see path (a) in Schemes 3 and 4). Under inert atmosphere the radicals recombine to the starting sulfides (path (e) in Scheme 3 and path (c) in Scheme 4) with rate constants of 10⁹ – 10¹⁰ M⁻¹·s⁻¹. On the other hand, aryl thiyl radicals react with oxygen affording aryl sulfonic acids (paths (d) and (f) in Schemes 3 and 4, respectively) with rate constants of 10⁶ – 10⁷ M⁻¹·s⁻¹ and these compounds are the main photoproducts formed during irradiation.

In the case of diphenyl sulfide ionization from the triplet state (path (b) in Scheme 3) gives Ph₂S⁺ that reacts smoothly with molecular oxygen (path (d)). This reaction occurs with bimolecular rate constants (k_{ox}) of 10⁷ M⁻¹·s⁻¹ affording intermediate Ph₂SOO⁺ that finally evolves to Ph₂SO in the presence of Ph₂S and an electron donor, e.g., superoxide ion (path (g)). Besides, under inert atmosphere, Ph₂S⁺ turns back to Ph₂S by an electron transfer process (path (c)) with bimolecular rate constants of 10¹⁰ M⁻¹·s⁻¹. Noteworthy, superoxide ion is formed during the irradiation of Ph₂S and operates as an electron carrier (see Scheme 3).

Oxidation of thioanisoles takes place by singlet oxygen sensitization (path (b) in Scheme 4) that arise from the triplet excited state of thioanisoles with ϕ_{Δ} of 0.10–0.15. Because thioanisoles are reactive with singlet oxygen, formation of the S-persulfoxide intermediates is the next reaction step (path (e)) that converts efficiently to the corresponding sulfoxides (path (f)). However, paths (h) and (i) (see Scheme 4) are the main pathways for the oxidation process under acid catalysis because

phenyl sulfinic acid is the catalyst that is formed during the irradiation of thioanisoles. In fact, acid catalysis accelerates the sensitized oxidation reaction and favors the regioselectivity of the oxidation reaction giving exclusively the corresponding sulfoxides.

Finally, the finding that C–S fragmentation and S-sulfoxidation of diaryl and aryl alkyl sulfides are competitive pathways under direct irradiation (310 nm) sheds some light on the photochemistry of thioethers.

EXPERIMENTAL DETAILS

Materials. Thioanisoles, diphenyl sulfide, diphenyl sulfoxide, dodecyl methyl sulfide, and benzene sulphyinic acid, benzene sulphinic acid, and perinaphthenone were commercial products. Sulfoxides and sulfones used as reference compounds were prepared via published procedures.²⁵ The dodecyl methyl sulfoxide was prepared via published procedures.²⁶

Photoreactions. The photoreactions were carried out by using 0.01 M solutions of the sulfides in different solvents (methanol, acetonitrile and dichloromethane). The solutions were contained in rubber stoppered, 1 cm diameter quartz tubes and a steam of dry oxygen saturated with the appropriate solvent was passed into the solution through a needle during 10 min. The quartz tubes were exposed to ten phosphor-coated 15 W lamps (Rayonet) emitting at 310 nm. The photooxidation reaction of diphenyl sulfides and thioanisole in the presence of Rose Bengal (in methanol) were carried out using 0.01 M solutions and were contained in rubber stoppered, 1 cm diameter Pyrex tubes. A steam of dry oxygen saturated with methanol was passed into the solution through a needle during 10 min. The solutions were irradiated with four visible 15 W lamps emitting at 528 nm. Co-oxidation experiments were carried out by using 0.01 M solutions of both sulfides according to the procedure above-described.

The products were determined by GC on the basis of calibration curves in the presence of undecane as the internal standard. The identification of benzenesulfonic acid was based on the comparison of the retention time of an authentic commercial sample by ionic chromatography. Potentiometric acid titrations (NaOH 0.1 M) have been followed by using an Orion mod. 250 potentiometer equipped with an Orion pH glass combined electrode mod 91–56. The titrations by using 0.1 M NaOH have been performed on 10 mL photolyzed solutions in MeOH diluted with 100 mL water.

Quenching Measurements. Rate constants for the quenching of singlet oxygen were obtained from the shortening of the $(O_2)^1\Delta_g$ emission lifetime at 1.27 μm in the presence of known amounts of sulfides in aerated $CDCl_3$. Singlet oxygen was generated by energy transfer to O_2 from the triplet state of perinaphthenone, populated by laser excitation (Nd:YAG laser, 532 nm). The near-IR luminescence of molecular oxygen was observed at 90° geometry through a 5 mm thick AR-coated silicon metal filter with wavelength pass $>1.1 \mu\text{m}$ and an interference filter at 1.27 μm by means of a preamplified (low-impedance) Ge photodiode cooled at 77 K (time resolution 300 ns). Second-order analysis of the emission decay was performed with the exclusion of the initial part of the signal, affected by scattered light, sensitizer fluorescence, and the formation profile of the emission signal itself. Comparison of the zero time intensity of the signal of the sulfides with that of the perinaphthone allowed measuring the production of singlet oxygen (ϕ_Δ).

Fluorescence Quantum Yield. UV and fluorescence spectra were recorded on a Jasco V-550 UV spectrophotometer and a PerkinElmer LSSS luminescence spectrometer, respectively. Fluorescence quantum yield (ϕ_f) were measured in acetonitrile and calculated by using 4-chloroanisole as fluorescence reference.¹⁹

Chemical Quantum Yield. The light flux was determined by irradiation of an aqueous solution of KI (0.6 M), KIO_3 (0.1 M) and $Na_2B_2O_7 \cdot 10H_2O$ (0.01 M) and measuring the formation of I_3^- by UV–visible spectroscopy after irradiation with ten phosphor-coated 15 W lamps (Rayonet) emitting at 310 nm ($\phi(I_3^-) = 0.38$).¹⁴

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Notes

The authors declare no competing financial interest.

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